Optical Resolution of a Co(III) Complex of 2-Hydroxy-1,3-propanediamine-*N,N,N′,N′*-tetraacetic Acid: Crystal Structure of (+)$_{589}$-Strychnine (2-Hydroxy-1,3-propanediamine-*N,N,N′,N′*-tetraacetato)-cobaltate(III) Sesquihydrate, (+)$_{589}$-(STC)-[Co(dhpta)]·1.5H$_2$O

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The 2-hydroxy-1,3-propanediamine-*N,N,N′,N′*-tetraacetatocobaltate(III) complex has been optically resolved using strychnine nitrate. The crystal structure of the optically active complex with the resolving agent, (+)$_{589}$-(STC)[Co(dhpta)]·1.5H$_2$O has been determined from three dimensional X-ray diffraction data. The absolute configuration around the cobalt atom, to which two nitrogen and four oxygen atoms in the ligand are bonded nearly octahedrally, is Δ. The six-membered chelate ring adopts the λ-skew boat conformation. The intermolecular hydrogen bonding between the coordinated oxygen atom of the acetate ring and the protonated nitrogen atom of strychnine, which is one of the asymmetric centers, plays an important role in the diastereomeric discrimination. In contrast, the non-coordinated hydroxyl group in the complex ion does not interact directly with the strychnine molecule. The relationship between the absolute configuration around the cobalt center and the circular dichroism has been examined for the optically active complex ion.

Optical resolution of racemic compounds, which has many empirical aspects, is an important area of chemistry. The optical resolution of the tetragonal Co(III) complex of 2,2′-bipiperidine, which has no net chirality around the central cobalt ion, has been attained by the organic resolving agent ammonium (+)-3-bromocamphor-9-sulfonate in our recent study.[1] By the crystal structure study of the complex having the resolving agent, we reported an indirect type of interaction between the complex cation and the resolving agent anion, implying the importance of the water molecules of crystallization and the asymmetric nitrogen centers caused by coordination,[2] as compared with the known type of direct interaction,[3] in the case of the (+)-3-bromocamphor-9-sulfonate salt. On the other hand, there is little information on the interaction between the anionic complex ion and the organic resolving agent.

Recently, by the preparation of the strychnine salt, the optically active Co(III) complex of 2-hydroxy-1,3-propanediamine-*N,N,N′,N′*-tetraacetic acid (DHPTA) was obtained, in which the carbon atom bonded to the hydroxyl group becomes an asymmetric center by coordination. Strychnine, which has eight asymmetric centers including two asymmetric nitrogen atoms, is a type of alkaloid and can be used as a cationic resolving agent. We report here the preparation and the optical resolution of the cobalt(III) complex of DHPTA, and to our knowledge, the first X-ray structure determination of a Co(III) complex having strychnine as a counter cation. We are interested in this hexadentate ligand, DHPTA, since the existence of the hydroxyl group may afford the opportunities for certain modification, including the tethering of the complex to silica surfaces and polymers.

The X-ray crystal structure study on the complex, (±)-K[Co(dhpta)], has been performed by Kalina et al.,[4] and they indicated that the non-coordinated hydroxyl group significantly interacts with the carboxyl groups in the neighbouring complex ions. Our purpose in undertaking the present X-ray structure determination was fourfold: to determine the absolute configuration around the cobalt center of the (+)$_{589}$-[Co(dhpta)]$^-$ ion, to elucidate the conformation of the six-membered chelate ring involving the *C*-substituted hydroxyl group in the optically active form; to clarify the interaction between the complex anion and the resolving reagent, i.e. the strychnine cation; and to examine relationships between CD curves and absolute configuration at the cobalt center of EDTA-type hexadentate ligands, where EDTA represents ethylenediaminetetraacetic acid.

Experimental

Measurements. The absorption (AB) spectra were recorded on a Shimadzu UV-240 spectrophotometer. The CD spectra were measured with a JASCO J-500A recording spectropolarimeter. These spectra were obtained in water. The ^{13}C NMR spectra were measured on a JEOL GNM JX-400 (400 MHz) spectrometer in D$_2$O, with dioxane as the internal standard. The optical rotations were measured in a 10 mm tube at 18 °C on a JASCO DIP-360 digital polarimeter.

Materials. All the reagents were of the best commercial grade and were used without further purification.

Preparation of K[Co(dhpta)]·0.5H$_2$O; 6.0 g of Na$_3$[Co(NO$_2$)$_6$] were dissolved in 30 ml of water. To the solution 5.0 g of 2-hydroxy-1,3-propanediamine-*N,N,N′,N′*-tetraacetic acid were added with stirring. The solution was heated on a water bath at 60 °C until the original orange-yellow color changed to deep purple. During the reaction, a deep purple complex was precipitated from the solution. After cooling to room temperature, the solution was kept in a refrigerator overnight. The rather insoluble sodium salt of the complex formed was filtered, washed with water, and dried in a desiccator. Yield; 4.90 g. In order to purify the compound, the countercation was changed from sodium to potassium as follows: A large amount of aqueous solution, in which the precipitate was dissolved, was poured onto a cation-exchange resin (Dowex50W-X2, K^+ form) packed in a column. The deep purple eluent from the column, which was flushed with water, was collected and evaporated under reduced pressure to 50 ml. The solution was allowed to stand in a refrigerator for a week, and the crystals formed were collected, washed with cold water, and dried in a desiccator. Found : C, 30.9; H, 3.39; N, 6.54%. Calcd for $C_{11}H_{15}N_2O_{9.5}CoK$: C, 31.1; H, 3.55; N, 6.59%. ^{13}C NMR (D_2O) δ=58.2, 60.6, 64.0, 64.8, 65.7, 69.9, 70.1, 181.2, 181.3, 182.8, and 183.4.

Optical Resolution: Preparation of (+)$_{589}$-(STC)[Co(dhpta)]·1.5H_2O. 1.72 g of K[Co(dhpta)]·0.5H_2O was dissolved in 50 ml of water at 60 °C. To the solution 0.90 g of strychnine nitrate was added as a resolving agent and the solution was warmed at the same temperature until complete dissolution was achieved. After filtration, the solution was kept in a refrigerater for a week. The deep purple prismatic crystals formed were collected, washed with cold water and air-dried. Yield; 0.91 g. The crystals formed after recrystallization in water at 60 °C, gave the same value of the ratio α (589 nm)/ε(absorption coefficient) as that of the crystals before recrystallization. Found: C, 52.0; H, 5.62; N, 7.46%. Calcd for $C_{32}H_{40}N_4O_{12.5}Co$: C, 52.0; H, 5.45; N, 7.58%.

Preparation of (+)$_{589}$-K[Co(dhpta)]·H_2O. (+)$_{589}$-(STC)[Co(dhpta)]·1.5H_2O was dissolved in water with sonicated stirring. The solution was poured into a column (45×2 cm) containing a cation-exchange resin (Dowex50W-X2, K^+ form). The column was flushed with water to elute the purple complex thoroughly. The eluted solution was collected and evaporated under reduced pressure to 20 ml. Twice this volume of methanol was gradually added to the solution, and then the solution was allowed to stand for overnight at ambient temperature. The resulting crystals were collected and washed with methanol, and dried under reduced pressure. Found: C, 31.5; H, 3.57; N, 6.60%. Calcd for $C_{11}H_{14}N_2O_9CoK$: C, 31.7; H, 3.39; N, 6.73%. $[\alpha]_D$=+874°(in 0.174% aqueous solution). $[M]_D$=+3638°.

Intensity Data Collection. The crystal employed in the data collection was a deep purple prism and bounded by (100), (001), and (010) faces. Crystal size 0.24×0.29×0.17 mm. The diffraction data were measured on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Unit cell and orientation parameters were determined on the basis of the setting angles of 28 carefully centered reflections (2θ=20—30°). Within the range of $2\theta<65°$, 3632 independent reflections with $F_o>5[\sigma(F_o)]$ were obtained. Intensities were measured by the ω-2θ scan method. Three check reflections, (3,0,0), (0,4,0), and (0,0,4), were measured every 50 reflections and no significant variation in intensities was found. Lorentz and polarization corrections were applied. An absorption correction was not performed because the absorption coefficient of the compound was low (μ=6.01 cm^{-1}).

Crystal data: Monoclinic, $P2_1$, a=15.536(3) Å, b=11.100(2) Å, c=9.339(2) Å, β=92.86(2)°, and Z=2, D_m=1.55, D_x=1.53 g cm^{-3}.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. All the nonhydrogen atoms except for the oxygen atoms of water molecules were located on a difference Fourier map. Subsequent difference Fourier calculations, phased with refined nonhydrogen atoms, gave the coordinates of the oxygen atoms of crystalline water and almost all the hydrogen positions except for those of the water molecules and some in the strychnine residue. Idealized coordinates of the remaining hydrogen atoms of the strychnine molecule were calculated

Table 1. Atomic Parameters for Non-Hydrogen Atoms, with Their Standard Deviations in Parentheses[a)]

Atom	x	y	z	B_{eq}
Co	1119(1)	2500(1)	3914(1)	1.8
O(1)	−86(3)	2837(5)	3851(6)	2.7
O(2)	−1199(4)	3132(8)	2329(8)	5.0
O(3)	1378(4)	4096(5)	3259(6)	2.9
O(4)	2037(5)	4995(7)	1534(8)	5.1
O(5)	1219(4)	2967(5)	5891(6)	2.7
O(6)	745(4)	2455(8)	8012(6)	3.5
O(7)	2311(3)	2159(5)	3962(6)	2.6
O(8)	3267(4)	800(9)	4675(10)	5.7
O(9)	−173(5)	−275(7)	1318(7)	4.3
O1	6674(4)	−4619(7)	9016(9)	5.0
O2	4556(4)	−1945(6)	7258(10)	5.7
OW1	7660(7)	−4816(11)	11596(10)	7.9
OW2	1776(12)	7523(24)	763(29)	10.8
N(1)	995(3)	2132(6)	1892(7)	2.0
N(2)	934(4)	870(6)	4673(6)	2.2
N1	5274(4)	−5101(7)	8464(8)	2.7
N2	2468(4)	−5280(6)	6600(8)	2.7
C(1)	1169(6)	845(8)	1532(9)	2.8
C(2)	620(6)	−117(8)	2200(9)	3.0
C(3)	324(5)	148(8)	3725(9)	2.8
C(4)	99(5)	2489(11)	1382(8)	2.8
C(5)	−446(5)	2858(8)	2584(9)	2.8
C(6)	1640(5)	2919(8)	1241(9)	2.7
C(7)	1684(6)	4102(8)	2079(9)	3.1
C(8)	514(6)	1100(8)	6077(9)	3.0
C(9)	861(5)	2261(7)	6741(8)	2.4
C(10)	1794(5)	284(8)	4907(9)	2.9
C2	4422(7)	−8112(8)	7718(11)	3.5
C(11)	2532(6)	1134(9)	4509(10)	3.3
C2	4422(7)	−8112(8)	7718(11)	3.5
C3	5139(8)	−8850(8)	8113(11)	4.0
C4	5926(7)	−8347(9)	8588(10)	3.7
C5	6036(6)	−7104(9)	8793(11)	3.5
C6	5340(5)	−6389(8)	8382(9)	2.8
C7	4440(4)	−4689(7)	7756(8)	2.0
C8	3885(5)	−5864(7)	7611(9)	2.4
C9	3320(5)	−5918(8)	6217(10)	2.9
C10	3680(6)	−5333(8)	4904(9)	2.9
C11	3911(5)	−4020(8)	5284(8)	2.3
C12	4671(4)	−4066(7)	6370(8)	2.0
C13	5123(5)	−2887(7)	6784(10)	2.8
C14	5732(6)	−3026(9)	8134(12)	3.7
C15	5963(5)	−4324(9)	8560(10)	3.2
C16	3945(7)	−1512(9)	6315(18)	6.5
C17	3124(5)	−2260(10)	6275(13)	4.4
C18	3111(5)	−3382(8)	5805(9)	2.5
C19	2312(5)	−4121(8)	5747(10)	3.1
C20	2501(5)	−5097(9)	8167(11)	3.3
C21	3196(5)	−5930(8)	8768(10)	3.0

a) Positional parameters are multiplied by 10^4.

by assuming a tetrahedral coordination about the carbon atoms with a C-H bond distance of 1.08 Å. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Refinement was carried out by use of a block-diagonal least-squares procedure. The atomic-scattering factors and the anomalous terms for Co, O, N, and C were taken from Ref. 5. The final indicies were R=0.063 and R'=0.072, where $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R'=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|)^{1/2}$; $w=1/[\sigma(F_o)]^2$. The final difference Fourier synthesis still showed peaks at heights up to 0.98 e Å^{-3} around the cobalt atom, and 0.68 e Å^{-3} around an oxygen atom of strychnine, although the electron density did not rise above 0.56 e Å^{-3} elsewhere. The final atomic coordinates along with their standard deviations and thermal parameters of non-hydrogen atoms are incorporated in Table 1. Compilations of the anisotropic thermal parameters for non-hydrogen atoms, atomic parameters for hydrogen atoms and observed and calculated structure factors are available.[6] All the calculations were performed on a HITAC M-680H computer at the Computer Center of the University of Tokyo with Universal Program System UNICS III.[7]

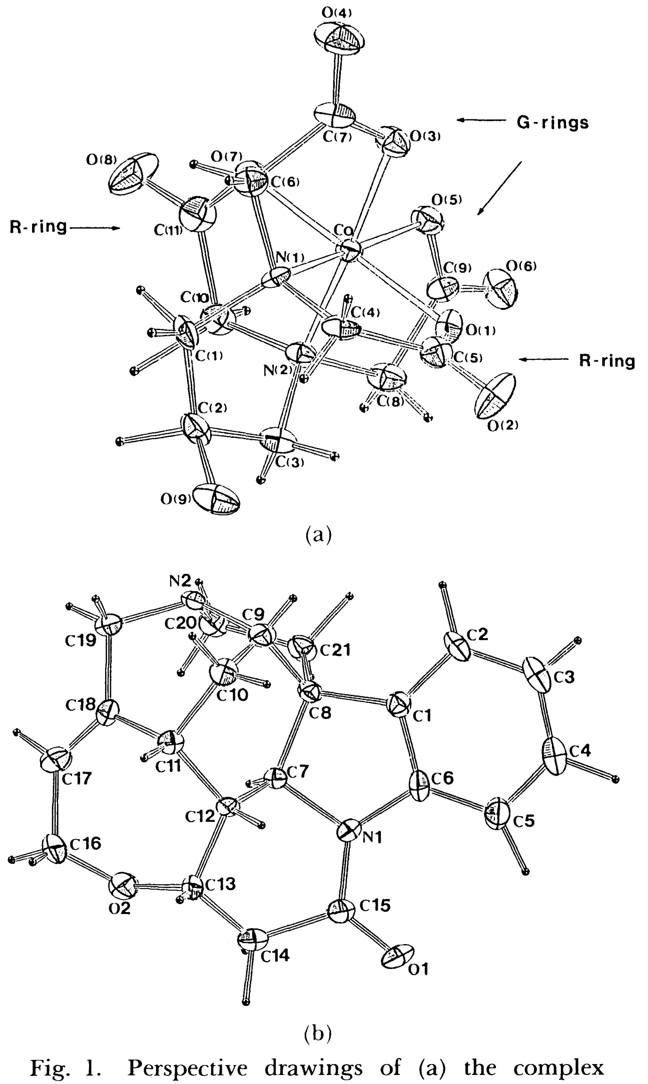
Results and Discussion

Preparation and Optical Resolution. The syntheses of Co(III) complexes coordinated by the hexadentate EDTA type ligands, for instance, ethylenediaminetetrapropionate (EDTP), trimethylenediaminetetraacetate (TNTA), propylenediaminetetraacetate (PDTA) and *trans*-1,2-cyclohexanediaminetetraacetate (CHXNTA) ions, have been well established. In each case, the potassium salt has been prepared in sufficient yield,[8–11] by application of the oxidation reaction from Co^{2+} in the presence of hydrogen peroxide and each ligand. On the other hand, the present complex, $K[Co(dhpta)]\cdot0.5H_2O$ was synthesized in sufficient yield by the substitution reaction from the starting material $Na_3[Co(NO_2)_6]$, whose cobalt ion is trivalent. In the case of the reaction of ethylenediaminetetraacetic acid disodium salt (Na_2H_2edta) with $Na_3[Co(NO_2)_6]$, it is known that the substitution reaction of the nitro groups occurs incompletely under similar conditions, and the complex, $Na_2[Co(NO_2)(Hedta)]\cdot2H_2O$ can be obtained in high yield.[12] In contrast, complete substitution was attained in the present case. This result may be related to the less strained ring system of the present complex having the central six-membered chelate ring. This assumption is supported by failure of attempts to prepare a complex in which trimethylenediaminetetraacetate functions as a pentadentate ligand.

The optical resolution of the ethylenediaminetetraacetatocobaltate(III), through its strychnine salt, was first attained by Busch and Bailar.[13] They obtained the active complex of the $(-)_{589}$-form by the fractionation from mixed solvents, because of the extreme solubility of the salt in water. The resolution of the present complex can be effected by strychnine, and the $(+)_{589}$-form of the complex was adequately obtained from water. Spontaneous resolution was reported by Ogino et al., in the case of $[Co(tnta)]^-$,[14] though in the present case no tendency to resolve spontaneously into optical isomers was observed.

Description of the Molecular Structure. Perspective drawings of the complex anion and strychnine cation showing ellipsoids of thermal motion are given in Fig. 1. Interatomic distances and angles are listed in Tables 2 and 3, respectively.

The cobalt atom is surrounded by two nitrogen atoms and four oxygen atoms from the four carboxyl groups at the apices of a slightly distorted octahedron. Each atom of the complex anion is inequivalent, because of the substituted hydroxyl group on the central carbon atom, through which the pseudo two-fold axis exists. This result agrees with the ^{13}C NMR spectrum of the inactive complex ion before resolution, which shows eleven signals for eleven carbon atoms (see Experimental section). The absolute configuration around the cobalt atom is Δ. This config-



(a)

(b)

Fig. 1. Perspective drawings of (a) the complex anion and (b) strychnine cation with their numbering schemes, shown as 50% probability ellipsoids.

uration was determined by reference of the known absolute configuration of the strychnine molecule used in the optical resolution. The central six-membered chelate ring adopts the λ-skew boat conformation, and both of the G- and R-rings have envelope conformations, where G- and R-rings represent the five-membered glycinate chelate rings as shown in Fig. 1.

The average Co-O bond length of the G-ring chelates and that of the R-ring chelates are 1.920(6) and 1.898(5) Å, respectively. Each of them is slightly long compared with the distances in (±)-K[Co(dhpta)] studied by Kalina et al.,[4] the average Co-O (G-ring) and Co-O (R-ring) distances being 1.875(9) and 1.887(9) Å, respectively. Moreover, in the present case, the average distance between cobalt and coordinated oxygen atoms in G-ring chelates is slightly longer than that in R-ring chelates, contrary to the previous correlation observed in (±)-K[Co(dhpta)]. This relation, between the Co-O bond distances of G-rings and those of R-rings, observed in the present complex ion is also found in the other complex ion of EDTA type ligands,[15–17] excent for the previous report.

X-Ray structure studies on EDTA type Co(III) complexes,[4,15–17] have indicated that the structure of the in-plane G-ring forming a girdle around the cobalt atom is more strained than that of the out-of-plane R-ring. The deviations of the atoms from the individual planes are listed in Table 4. Pronounced deviations are observed of the C(6), C(7), C(8), and C(9) atoms, of which the G-ring chelates consist, whereas the displacements of the carbon atoms in the R-rings from the mean planes are not so significant. Each glycinate ring of the present complex ion is less deformed from defined planes than that of the complex ion previously reported,[4] except for one G-ring,

Table 2. Bond Distances (l/Å)[a]

(a) Complex anion			
Co-O(1)	1.906(5)	Co-O(3)	1.923(6)
Co-O(5)	1.917(6)	Co-O(7)	1.889(5)
Co-N(1)	1.933(6)	Co-N(2)	1.969(7)
O(1)-C(5)	1.284(10)	O(2)-C(5)	1.221(10)
O(3)-C(7)	1.222(11)	O(4)-C(7)	1.254(12)
O(5)-C(9)	1.264(10)	O(6)-C(9)	1.229(9)
O(7)-C(11)	1.287(11)	O(8)-C(11)	1.205(11)
O(9)-C(2)	1.458(11)		
N(1)-C(1)	1.494(11)	N(1)-C(4)	1.501(9)
N(1)-C(6)	1.483(10)	N(2)-C(3)	1.497(11)
N(2)-C(8)	1.515(11)	N(2)-C(10)	1.492(11)
C(1)-C(2)	1.520(12)	C(2)-C(3)	1.547(13)
C(4)-C(5)	1.497(12)	C(6)-C(7)	1.528(13)
C(8)-C(9)	1.517(12)	C(10)-C(11)	1.544(13)
(b) Strychnine cation			
O1-C15	1.210(11)	O2-C13	1.451(11)
O2-C16	1.350(16)		
N1-C6	1.436(11)	N1-C7	1.497(9)
N1-C15	1.373(11)	N2-C20	1.476(12)
N2-C9	1.558(11)	N2-C19	1.526(12)
C1-C2	1.400(12)	C1-C6	1.409(11)
C1-C8	1.527(11)	C2-C3	1.417(14)
C3-C4	1.397(15)	C4-C5	1.402(14)
C5-C6	1.380(13)	C7-C8	1.565(11)
C7-C12	1.526(11)	C8-C9	1.535(12)
C8-C21	1.560(12)	C9-C10	1.518(13)
C10-C11	1.538(12)	C11-C12	1.519(10)
C11-C18	1.531(11)	C12-C13	1.526(11)
C13-C14	1.546(13)	C14-C15	1.532(14)
C16-C17	1.520(14)	C17-C18	1.320(14)
C18-C19	1.488(12)	C20-C21	1.509(12)

a) Estimated standard deviations in parentheses.

Table 3. Bond Angles (ϕ/°)[a]

(a) Complex anion			
O(1)-Co-O(3)	91.7(3)	O(1)-Co-O(5)	90.6(2)
O(1)-Co-O(7)	179.5(3)	O(1)-Co-N(1)	87.8(2)
O(1)-Co-N(2)	91.8(3)	O(3)-Co-O(5)	92.8(3)
O(3)-Co-O(7)	88.4(3)	O(3)-Co-N(1)	84.0(3)
O(3)-Co-N(2)	175.7(3)	O(5)-Co-O(7)	89.9(2)
O(5)-Co-N(1)	176.4(3)	O(5)-Co-N(2)	84.7(3)
O(7)-Co-N(1)	91.8(2)	O(7)-Co-N(2)	88.1(3)
N(1)-Co-N(2)	98.5(3)		
Co-O(1)-C(5)	114.5(5)	Co-O(3)-C(7)	112.9(6)
Co-O(5)-C(9)	114.8(5)	Co-O(7)-C(11)	115.4(5)
Co-N(1)-C(1)	114.3(5)	Co-N(1)-C(4)	107.4(4)
Co-N(1)-C(6)	103.8(5)	Co-N(2)-C(3)	112.2(5)
Co-N(2)-C(8)	103.5(5)	Co-N(2)-C(10)	108.0(5)
O(1)-C(5)-O2)	123.6(8)	O(3)-C(7)-O(4)	124.6(9)
O(5)-C(9)-O(6)	126.1(8)	O(7)-C(11)-O(8)	123.8(9)
O(1)-C(5)-C(4)	116.7(7)	O(2)-C(5)-C(4)	119.7(8)
O(3)-C(7)-C(6)	116.6(8)	O(4)-C(7)-C(6)	118.8(8)
O(9)-C(2)-C(1)	109.2(7)	O(9)-C(2)-C(3)	105.2(7)
C(1)-N(1)-C(4)	110.9(7)	C(1)-N(1)-C(6)	109.7(6)
C(4)-N(1)-C(6)	110.4(6)	C(3)-N(2)-C(8)	108.3(6)
C(3)-N(2)-C(10)	112.9(6)	C(8)-N(2)-C(10)	111.6(6)
N(1)-C(1)-C(2)	117.9(7)	N(1)-C(4)-C(5)	112.6(6)
N(1)-C(6)-C(7)	108.1(7)	N(2)-C(3)-C(2)	116.0(7)
N(2)-C(8)-C(9)	109.7(7)	N(2)-C(10)-C(11)	111.6(7)
C(1)-C(2)-C(3)	116.3(7)		
(b) Strychnine cation			
O1-C15-N1	123.2(9)	O1-C15-C14	122.9(9)
C13-O2-C16	118.4(10)	O2-C13-C12	114.6(6)
O2-C13-C14	100.4(8)	O2-C16-C17	112.5(10)
N1-C6-C1	109.3(7)	N1-C6-C5	127.9(8)
N1-C7-C8	104.2(6)	N1-C7-C12	106.1(6)
C6-N1-C7	110.1(6)	C6-N1-C15	124.8(7)
C7-N1-C15	119.5(7)	C9-N2-C19	112.2(6)
C9-N2-C20	107.7(6)	C19-N2-C20	113.4(7)
C2-C1-C6	121.2(8)	C2-C1-C8	128.1(7)
C6-C1-C8	110.3(7)	C1-C2-C3	116.3(9)
C2-C3-C4	121.0(9)	C3-C4-C5	122.4(9)
C4-C5-C6	116.1(8)	C1-C6-C5	122.7(8)
C8-C7-C12	117.2(6)	C1-C8-C7	103.3(6)
C1-C8-C9	116.3(7)	C7-C8-C9	113.3(7)
C1-C8-C21	110.7(7)	C7-C8-C21	112.0(7)
C21-C8-C9	101.7(6)	C8-C9-C10	116.8(7)
C9-C10-C11	108.0(7)	C10-C11-C12	106.7(6)
C10-C11-C18	109.2(7)	C12-C11-C18	114.8(6)
C7-C12-C11	111.9(6)	C7-C12-C13	107.4(7)
C11-C12-C13	118.3(7)	C12-C13-C14	112.1(7)
C13-C14-C15	115.6(8)	C16-C17-C18	121.5(9)
C11-C18-C17	122.9(7)	C11-C18-C19	115.0(7)
C17-C18-C19	122.1(8)	C8-C21-C20	102.5(7)

a) Estimated standard deviations in parentheses.

i.e., the C(8) and C(9) atoms deviate 0.70 and 0.45 Å, respectively from the equatorial plane, the corresponding values being 0.62 and 0.17 Å, respectively.

The other bond distances and angles of the present complex ion are almost comparable with the reported values for (±)-K[Co(dhpta)], except for the relationship described above and of characteristics for the Co(III) complexes of EDTA type ligands. According to the structural study on the Co(III) complexes of EDTA type ligands, which functions as a pentadentate ligand,[18] the relationship mentioned above may be significant, because the coordination site corresponding to one G-ring is substituted by a monodentate ligand in those cases. Easier bond cleavage of Co–O bonds of G-rings than those of R-rings can be interpreted by the correlation.

The structure of the strychnine cation, used as the resolving agent, agrees with the known absolute configurations, and the stereochemistry is almost identical with that previously reported on the molecule and its derivatives.[19]

Description of the Unit Cell and Diastereomeric Discrimination. A perspective drawing of the crystal structure viewed along the b axis is presented in Fig. 2. The unit cell consists of two complex anions, two strychnine counterions, and the four water molecules of crystallization.

Hydrogen bonds of the type O–H···O probably exist between the O(6) atom of the non-coordinated oxygen atom in one G-ring chelate and the O(9) atom of the hydroxyl group in the neighboring complex anion, the O···O distance being 2.75 Å. Such a strong intermolecular hydrogen bond of the same manner was observed in (±)-K[Co(dhpta)]. The O(2) atom of the carboxylato group in one R-ring, which is not coordinated to the cobalt atom, is not only linked to the oxygen OW1 atom of the water but also associated to the other water OW2 atom, by an O–H···O hydrogen bond of distances 2.95 and 3.06 Å respectively. The two water molecules are not connected to any other atoms. In the crystal structures of potassium salts of $(+)_{546}$-[Co(tnta)]$^-$ and (±)-[Co(dhpta)]$^-$, the cationic potassium ions are surrounded through electrostatic attraction by the uncoordinated carboxylate oxygen atoms and also the oxygen atoms of water molecules in defined[15] and nondifined[4] arrangements, respectively. Such a rigid network of electrostatic attraction found in the previous reports, however, among the complex anion, the strychnine, and the water

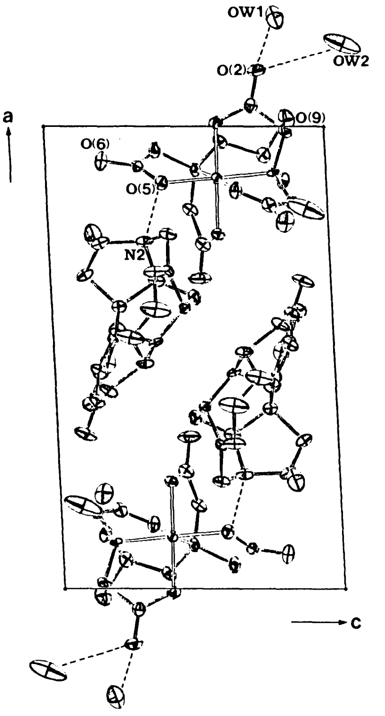


Fig. 2. Perspective drawing of the crystal structure viewed along the b axis. The significant hydrogen bonds among the complex anion, strychnine cation, and water molecules are indicated by the broken line, except for that between O(6) and O(9) atoms.

Table 4 Deviations of the Atoms from Planes

Plane, No.	Atoms defining the plane	Out-of-plane atoms	Distances between out-of-plane atoms, l/Å
	N(1)	C(1)	−0.54
1	Co	C(2)	0.14
	N(2)	C(3)	0.73
	Co	C(2)	0.13
	O(3)	C(6)	−0.78
2[a]	O(5)	C(7)	−0.56
	N(1)	C(8)	0.70
	N(2)	C(9)	0.45
	Co	C(4)	−0.21
3	O(1)	C(5)	−0.18
	N(1)		
	Co	C(10)	−0.04
4	O(7)	C(11)	−0.09
	N(2)		

a) Plane defined by least-square procedure.

molecules can not be observed in the present case.

Significantly the coordinated O(5) atom, of which the same G-ring of the O(6) atom connecting with the O(9) atom of the neighboring complex ion by hydrogen bond consists, is associated with the nitrogen atom N2 of the strychnine cation with an N···O distance of 2.80 Å, by an N-H···O hydrogen bond. It is assumed that a hydrogen atom may be attached to the N(2) atom of the strychnine molecule, though examination of the difference fourier map was unable to reveal a possible hydrogen position near the N2 atom.

The O(2), O(3), and O(4) atoms of the complex ion are near the hydrogen atoms bonded to the carbon atoms of strychnine around the N2 atom, the O···H distances ranging from 2.37 to 2.98 Å, as the result of the hydrogen bond between the O(5) atom of the complex anion and the N2 atom of the strychnine molecule, mentioned above. Moreover, the carbon and hydrogen atoms belonging to the benzene residue of the strychnine interact with the other hydrogen atoms in the hydrophilic sphere of the neighboring strychnine, showing distances from 2.58 to 3.01 Å for C···H intermolecular interaction and from 2.40 to 3.08 Å for H···H interaction, though the self-stacking of the benzene residue of the strychnine molecule can not be observed.

Thus, the close contact by the possible hydrogen bond between the O(5) atom of the complex anion and the N2 atom of the strychnine molecule may play an important role in the diastereomeric discrimination in the present complex, since the N2 atom is one of the asymmetric centers in the strychnine molecule. On the other hand, the O(9) atom of the hydroxyl group bonding to the C(2) carbon atom, which is a resulting asymmetric center by coordination, does not interact directly with the strychnine molecule by an obvious hydrogen bond, though the atom forms the hydrogen bond network together with the O(6) atom in the same G-ring of the O(5) atom. The close contacts between the benzene residue and the atoms in hydrophilic sphere of the neighboring strychnine molecule, described above, probably assist in formation of the diastereomeric compound, i.e., in the optical resolution of the complex.

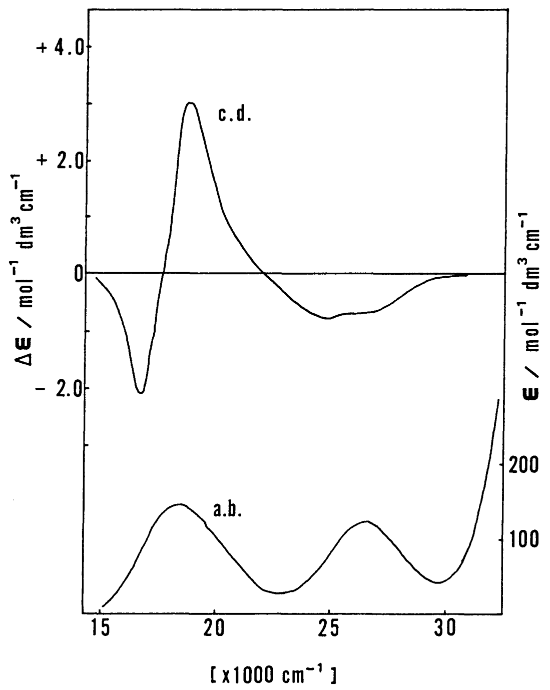


Fig. 3. Absorption and circular dichroism spectra of $(+)_{589}$-Δ-K[Co(dhpta)] in H$_2$O.

Table 5. Absorption and Circular Dichroism Data for $(+)_{589}$-Δ-K[Co(dhpta)], with Those for $(-)_{546}$-Λ-Na[Co(tnta)]·3H$_2$O in Parentheses[a)]

Absorption Peak position, ×1000 cm^{-1}	ε	Circular dichroism Peak position, ×1000 cm^{-1}	$\Delta\varepsilon$
18.25 (18.20)	142 (131)	16.72 (17.00)	−2.12 (+1.91)
		18.73 (19.00)	+3.01 (−2.41)
26.46 (26.40)	121 (115)	24.39 (24.60)	−0.80 (+0.69)

a) References 8 and 13.

Absolute Configuration and Circular Dichroism. The AB and CD spectra of the present complex ion $(+)_{589}$-[Co(dhpta)]$^-$ are shown in Fig. 3. Numerical data are summarized in Table 5, along with those of the $(-)_{546}$-[Co(tnta)]$^-$ ion. The shape and positions of AB and CD spectra of the present $(+)_{589}$-form complex are quite similar to those of $(+)_{546}$-[Co(tnta)]$^-$ reported by Ogino et al.[14)] X-Ray structure analysis and circular dichroism studies of the series of EDTA type complex, whose CD spectra usually show two Cotton effects of opposite sign in the first absorption region, suggest the following empirical rule: The sign of the CD band in the region can be related to the configuration around the cobalt centers. When they give a positive and negative Cotton effect respectively from the lower energy band of the first absorption region, they should be assigned to the Λ configuration around the asymmetric cobalt center. In the CD spectrum of $(+)_{589}$-[Co(dhpta)]$^-$, which was derived from the crystals of the present work, a negative and a positive Cotton effect has been observed, from the lower energy band in the region. The absolute configuration of the cobalt atom has been determined as Δ from the present study. Consequently, the empirical rule appears to be applicable to the series of EDTA type complex, even though the hydroxyl group exists in the central chelate ring.

Conclusion

Optical resolution of the 2-hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetatocobaltate(III) complex ion has been accomplished by the organic resolving agent, strychnine. By the X-ray structure study on the crystal involving the resolving agent, the oxygen atom coordinated to the cobalt ion plays an important role in the diastereomeric discrimination through the O···H–N type of hydrogen bond, though the non-coordinated hydroxyl group does not interact directly with strychnine in the same manner. This fact suggests that the coordinated oxygen atom in the G-ring is an essential site for the discrimination of the form of a compound by the complex and certain modification of the corresponding hydroxyl group may not prevent the optically active complex from functioning as a discriminator. The chemical modification of the hydroxyl group in the complex is now in progress.

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